

## **GAS CHROMATOGRAPHY -- GAS**

### **Introduction**

Hydrocarbon generation is the natural result of the maturation of buried organic matter. The sources of organic matter in ocean sediments include plankton, bacteria and land-derived material. The organic matter can be transformed into hydrocarbons, depending on burial depth and temperature. Hydrocarbons such as methane, ethane, propane and butane are usually found in the gaseous phase in sediments close to the surface. Microbial activity is most often the source of these gases at shallow depths, but one of the exciting discoveries of the Ocean Drilling Program (ODP) was evidence of microbial activity deeper in the crust.

Hydrocarbon monitoring was one of the primary reasons for the gas sampling and analysis. During the ODP, the *JOIDES Resolution* (*JR*) was not designed to drill in areas where oil or gas could be encountered. Proposed sites were intensively studied and reviewed in order to ensure those sites did not have factors conducive to hydrocarbon accumulation. Headspace gas samples and gas from expansion voids were analyzed as part of an active monitoring program. In addition to hydrocarbons, gases such as hydrogen sulfide represented a potential safety problem.

### **Data Acquisition**

Gas analyses were done on headspace samples (gas obtained from sediment samples) and vacutainer samples (void pockets within the core before the liner had been breached). Headspace samples (HS) were taken from the core immediately after the core was brought on deck. A 5 cm<sup>3</sup> sample was placed in a glass vial, sealed and heated for 30 minutes. A 5 ml volume of gas was extracted and analyzed with a gas chromatograph.

Vacutainer samples (VAC) were also taken immediately after the core came on deck if there were gas pockets, bubbling or frothing within the liner, or bulging end caps. A liner penetrator tool equipped with a valve and needle was used to collect gas samples. A pre-evacuated sealed glass tube or syringe was placed on the valve and the valve was opened for a few seconds. In the lab, some of the gas was extracted from the tube or syringe and analyzed with a gas chromatograph.

Over the span of the ODP, there were several instruments used to analyze the headspace and vacutainer gasses. Several Hewlett-Packard gas chromatographs have been used -- from the HP 5890A GC used during the early part of ODP to the HP 6890 GC instruments in the lab at the end of ODP. Instrumentation in the Chemistry Laboratory usually included a gas chromatograph with both flame ionization detectors (FID) and thermal conductivity detectors (TCD), a gas chromatograph with the Natural

Gas Analyzer (NGA), FID, and TCD. A Carle Series 100 Analytical Gas Chromatograph was used for rapid determinations of methane, ethane and propane.

Preanalyzed standards were run to ensure the chromatographic responses were calibrated. The calibration measurements were not archived or entered into the Janus database. Additional information about ODP gas analyses can be found in *Technical Note 30: Introduction to Shipboard Organic Geochemistry on the JOIDES Resolution*.

## Archive

### Pre-Janus Archive

Early in the ODP, gas data were collected on logsheets which were sent back to ODP/TAMU at the end of each cruise. The data were entered into an S1032 database and the logsheets were microfilmed for archival storage. Data entry routines were implemented so that data entry could be done on the ship and the practice of collecting data on logsheets ended. Gas analyses were stored in the S1032 database until the Janus database became operation on Leg 171.

### Migration of Gas Elements analyses to Janus

The data model for Gas Elements data can be found in Appendix I. Included are the relational diagram and the list of the tables that contain data pertinent to gas analyses, the column names and the definition of each column attribute. ODP Information Services Database Group was responsible for the migration of pre-Leg 171 data to Janus.

### Janus Gas Elements Data Format

Gas analyses can be retrieved from Janus Web using a predefined query. The Gas Elements query webpage allows the user to extract data using the following variables to restrict the amount of data retrieved: leg, site, hole, core, section, depth range, or latitude and longitude ranges. The gas query also gives the user the option of extracting data by sampling method, instrument used to analyze the gas or the detector type.

Table 1 contains the data fields retrieved from the Janus database using the Janus Web predefined query. The first column contains the data item; the second column indicates the Janus table or tables in which the data were stored; the third column is the Janus column name or the calculations used to produce the value. Appendix II contains additional information about the fields retrieved using the Janus Web Gas Elements query, and the data format for the archived ASCII files.

Table 2. Gas Elements query

| <b>Item Name</b>                   | <b>Janus Table</b> | <b>Janus Column Name or Calculation</b>          |
|------------------------------------|--------------------|--|
| Leg                                | SECTION            | Leg  |
| Site                               | SECTION            | Site   |
| Hole                               | SECTION            | Hole   |
| Core                               | SECTION            | Core   |
| Type                               | SECTION            | Core_type  |
| Section                            | SECTION            | Section_number                                   |
| Top (cm)                           | SAMPLE             | Top_interval * 100                               |
| Bottom (cm)                        | SAMPLE             | Bottom_interval *100                             |
| Depth (mbsf)                       | DEPTH_MAP, SAMPLE  | DEPTH_MAP.Map_interval_top + SAMPLE.Top_interval |
| Methane/Ethane (C1/C2 ratio)       | CHEM_GAS_ANALYSIS  | Calculated                                       |
| Methane (C1) [ppm]                 | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - C1::GAS_ANALYSIS_RESULT      |
| Ethane (C2) [ppm]                  | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - C2::GAS_ANALYSIS_RESULT      |
| Ethylene (C2=) [ppm]               | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - C2=:GAS_ANALYSIS_RESULT      |
| Ethane + Ethylene (C2+C2=) [ppm]   | CHEM_GAS_ANALYSIS  | Calculated                                       |
| Propane (C3) [ppm]                 | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - C3::GAS_ANALYSIS_RESULT      |
| Propane + Propylene (C3+C3=) [ppm] | CHEM_GAS_ANALYSIS  | Calculated                                       |
| Propylene (C3=) [ppm]              | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - C3=:GAS_ANALYSIS_RESULT      |
| i-Butane (I-C4) [ppm]              | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - I-C4::GAS_ANALYSIS_RESULT    |
| n-Butane (N-C4) [ppm]              | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - N-C4::GAS_ANALYSIS_RESULT    |
| n-Pentane (N-C5) [ppm]             | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - N-C5::GAS_ANALYSIS_RESULT    |
| i-Pentane (I-C5) [ppm]             | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - I-C5::GAS_ANALYSIS_RESULT    |
| n-Hexane (N-C6) [ppm]              | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - N-C6::GAS_ANALYSIS_RESULT    |
| i-Hexane (I-C6) [ppm]              | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - I-C6::GAS_ANALYSIS_RESULT    |
| n-Heptane (N-C7) [ppm]             | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - N-C7::GAS_ANALYSIS_RESULT    |
| i-Heptane (I-C7) [ppm]             | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - I-C7::GAS_ANALYSIS_RESULT    |
| Nitrogen (N2) [ppm]                | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - N2::GAS_ANALYSIS_RESULT      |
| Oxygen (O2) [ppm]                  | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - O2::GAS_ANALYSIS_RESULT      |
| Hydrogen Sulfide (H2S) [ppm]       | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - H2S::GAS_ANALYSIS_RESULT     |
| Carbon Dioxide (CO2) [ppm]         | CHEM_GAS_ANALYSIS  | GAS_ANALYSIS_CODE - CO2::GAS_ANALYSIS_RESULT     |
| Run                                | CHEM_GAS_SAMPLE    | Run_ID   |
| Instrument                         | CHEM_GAS_SAMPLE    | Method_code                                      |
| Method                             | CHEM_GAS_SAMPLE    | Gas_sample_method                                |
| Detector                           | CHEM_GAS_SAMPLE    | Gas_detector_signal                              |

## Data Quality

The collection of gas data was vitally important to the safety of drilling operations on the *JR*. A lot of care was taken in order to get rapid, accurate results. There are few known instances where there was a major problem with data collection. Anything written or typed was a potential source of errors. Analytical results were written on logsheets. These data were then typed into S1032. Data entry programs were implemented to add the data to S1032, but it still required manual entry. Typographical errors, writing or

typing incorrect information occasionally happened, and some mistakes were not identified. Often, the scientific party found errors and corrected them for the data included in the Initial Report volume, but data sent back to ODP/TAMU did not get corrected.

Another error found during the migration of gas data was that samples were missing from the database. In those instances, a sample was entered into the database so that the data could be migrated. The verification of those samples and the verification of the entire gas data set were not completed due to time constraints. Most data collected after the Janus database was operational on Leg 171 were verified as part of the Janus data management and verification procedures (see Metadata Introduction). Some verification was done on the pre-Leg 171 data; however, if there is a discrepancy between the database and data in the Initial Report volumes, the published data should be considered more reliable.

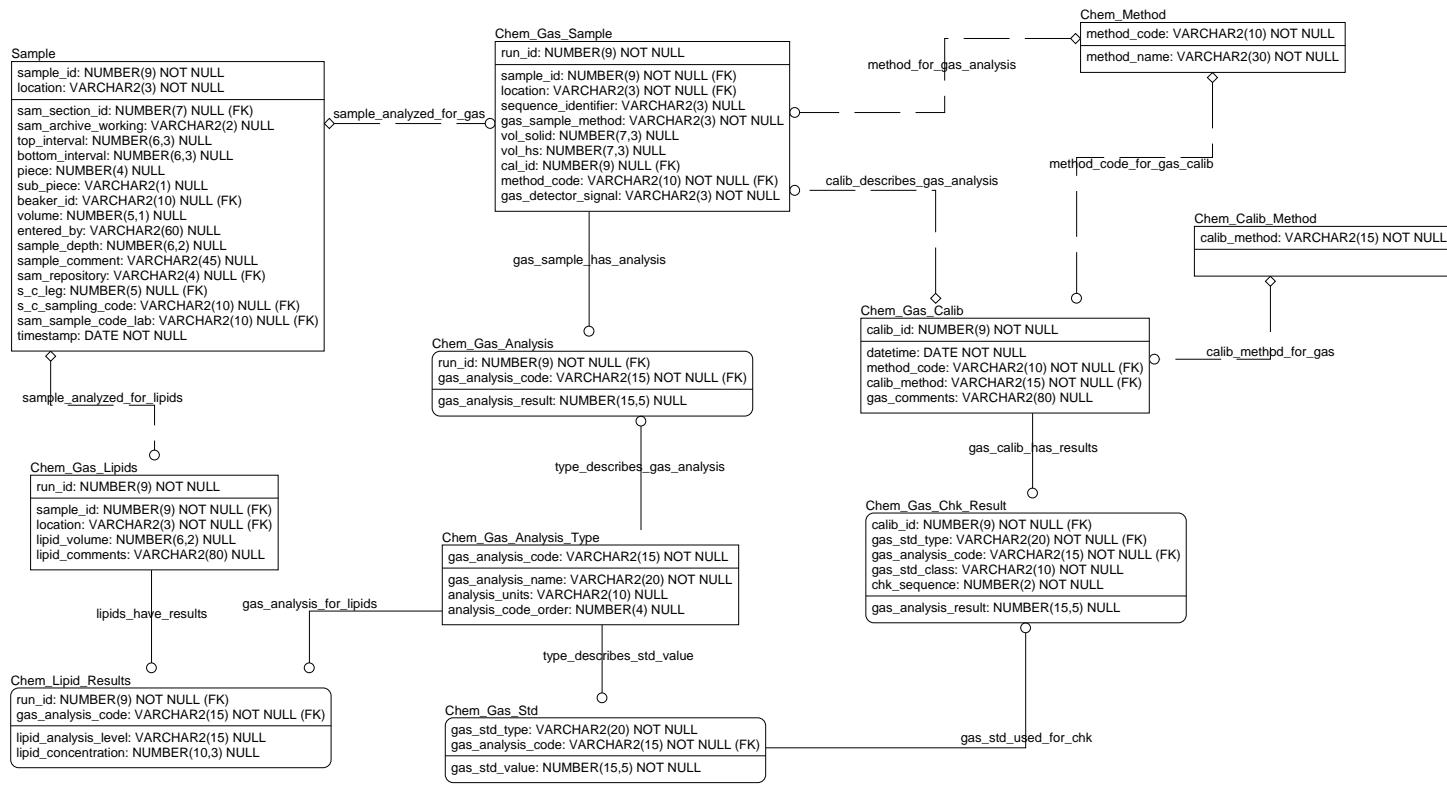
Janus does not contain any calibration information for the gas chromatography instrumentation. Procedures for collecting and storing calibration information in the database were not implemented during the ODP. Procedures for collecting data on lipids were also not implemented during the ODP.

## References

Emeis, K., and Kvenvolden, K.A., 1986. Shipboard Organic Geochemistry on *JOIDES Resolution*, ODP Tech. Note No. 7.

Kvenvolden, K.A., and McDonald, T.J., 1986. Organic Geochemistry on the *JOIDES Resolution*--An Assay, ODP Tech. Note No. 6.

Pimmel, A., and Claypool, G., 2001, Introduction to Shipboard Organic Geochemistry on the *JOIDES Resolution*. ODP Tech. Note 30.



## APPENDIX I: Janus Data Model – Gas Chromatography

| <b>Gas Chromatography</b>     |                      |  |
|-------------------------------|----------------------|--|
| <b>Table Name</b>             | <b>Column Name</b>   | <b>Column Comment</b>  |
| <b>Chem_Gas_Sample</b>        | run_id               | Unique Oracle-generated sequence identifier that will allow duplicate analyses from a sample to be entered into database.                      |
|                               | sample_id            | Oracle-generated sequence number that with <i>location</i> uniquely identifies a sample.   |
|                               | location             | Code that indicates which Janus application assigned the sample_id. Used with <i>sample_id</i> to uniquely identify a sample.                  |
|                               | sequence_identifier  | Number indicating order in which analyses were run when duplicate analyses are stored.   |
|                               | gas_sample_method    | The method used for obtaining a gas sample. HS = Headspace Sample, VAC = Vacutainer sample, O = Other.   |
|                               | vol_solid            | The volume of solid to be analyzed in milliliters.   |
|                               | vol_hs               | The volume of the headspace sample to be analyzed in milliliters. Volume of the headspace equals volume of the vial minus volume of the solid. |
|                               | cal_id               | Oracle-generated sequence number for a gas calibration run.  |
|                               | method_code          | A code for the method or instrument used to analyze a sample.  |
|                               | gas_detector_signal  | The type of signal. Valid values are: FID -- Flame Ionization Detector and TCD – Thermal Conductivity Detector.                                |
| <b>Chem_Gas_Analysis</b>      | run_id               | Unique Oracle-generated sequence identifier that will allow duplicate analyses from a sample to be entered into database.                      |
|                               | gas_analysis_code    | Code describing the type of analysis for which a gas sample was analyzed.  |
|                               | gas_analysis_result  | Numerical result of the analysis of a gas sample.  |
| <b>Chem_Gas_Analysis_Type</b> | gas_analysis_code    | Code describing the type of analysis for which a sample can be analyzed.   |
|                               | gas_analysis_name    | Full name or description of the gas analysis.  |
|                               | analysis_units       | The reported measurement units of the analysis result.   |
|                               | analysis_code_order  | Number defining the order that analysis codes and results will appear on a spreadsheet or report.  |
| <b>Chem_Method</b>            | method_code          | A code for the method or instrument used for analyzing a sample.   |
|                               | method_name          | The name of the method or instrument used for analyzing a sample   |
| <b>Chem_Gas_Lipids</b>        | run_id               | Unique Oracle-generated sequence identifier that will allow duplicate analyses from a sample to be entered into database.                      |
|                               | sample_id            | Oracle-generated sequence number that with <i>location</i> uniquely identifies a sample.   |
|                               | location             | Code that indicates which Janus application assigned the sample_id. Used with <i>sample_id</i> to uniquely identify a sample.                  |
|                               | lipid_volume         | The volume of a lipid sample, in microliters.  |
|                               | lipid_comments       | Comment concerning a sample analyzed for lipids.   |
| <b>Chem_Lipid_Results</b>     | run_id               | Unique Oracle-generated sequence identifier that will allow duplicate analyses from a sample to be entered into database.                      |
|                               | gas_analysis_code    | Code describing the type of analysis for which a gas sample was analyzed.  |
|                               | lipid_analysis_level | The amount of lipids in a sample. Valid values are: Major, Minor, Trace, Not Present, and Not Determined.                                      |
|                               | lipid_concentration  | The concentration of a lipid, derived from GC2 output.   |
| <b>Chem_Gas_Calib</b>         | calib_id             | Oracle-generated sequence number for a gas calibration run.  |
|                               | datetime             | Timestamp for calibration run.   |
|                               | method_code          | A code for the method or instrument being calibrated.  |
|                               | calib_method         | Method used for calibrating the analytical instrument.   |
|                               | gas_comments         | Comments concerning a gas calibration.   |
| <b>Chem_Calib_Method</b>      | calib_method         | Method used for calibrating analytical instruments.  |

## Gas Chromatography

| Table Name                 | Column Name            | Column Comment  |
|----------------------------|------------------------|---|
| <b>Chem_Gas_Chk_Result</b> | calib_id               | Oracle-generated sequence number for a gas calibration run.   |
|                            | gas_std_type           | The name or type of standard used for calibration or control run.   |
|                            | gas_analysis_code      | Code describing the type of analysis for which a gas standard was analyzed.   |
|                            | gas_std_class          | Defines the standard as a standard, a blank, or an unknown check.   |
|                            | chk_sequence           | Identifies the order of measurements.   |
|                            | gas_analysis_result    | Numerical result of the analysis of a gas sample.   |
| <b>Chem_Gas_Std</b>        | gas_std_type           | The name or type of standard used for a gas calibration.  |
|                            | gas_analysis_code      | Code describing the type of analysis for a gas standard.  |
|                            | gas_std_value          | The numerical value for a gas standard.   |
| <b>Section</b>             | section_id             | Unique Oracle-generated sequence number to identify each section. This is done because of the physical subsection / zero section problems. In adding new sections, deleting sections or changing sections - don't want to have to renumber.                           |
|                            | leg                    | Number identifying the cruise for which data were entered into the database.  |
|                            | site                   | Number identifying the site from which the core was retrieved. A site is the position of a beacon around which holes are drilled.   |
|                            | hole                   | Letter identifying the hole at a site from which a core was retrieved or data were collected.   |
|                            | core                   | Sequential numbers identifying the cores retrieved from a particular hole. Cores are generally 9.5 meters in length, and are numbered serially from the top of the hole downward.   |
|                            | core_type              | A letter code identifying the drill bit/coring method used to retrieve the core.  |
|                            | section_number         | Cores are cut into 1.5 m sections. Sections are numbered serially, with Section 1 at the top of the core.   |
|                            | section_type           | Used to differentiate sections of core (S) from core catchers (C). Previously core catchers were stored as section CC, but in Janus core catchers are given the next sequential number from the last section recovered.   |
|                            | curated_length         | The length of the section core material, in meters. This may be different than the liner length for the same section. Hard rock cores will often have spacers added to prevent rock pieces from damaging each other.  |
|                            | liner_length           | The original length of core material in the section, in meters. Sum of liner lengths of all the sections of a core equals core recovery.  |
|                            | core_catcher_stored_in | Sometimes the core catcher is stored in a D tube with a section. core_catcher_stored_in contains the section number of the D tube that holds the core catcher.  |
|                            | section_comments       | Comments about this section   |
| <b>Sample</b>              | sample_id              | Oracle-generated sequence number that with <i>location</i> uniquely identifies a sample.  |
|                            | location               | Code that indicates which Janus application assigned the sample_id. Values are SHI (ship), GCR (Gulf Coast Repository), ECR (East Coast Repository), WCR (West Coast Repository) and BCR (Bremen Core Repository). Used with sample_id to uniquely identify a sample. |
|                            | s_c_leg                | Number identifying the cruise for which data were entered into the database. Foreign key used with s_c_sampling_code to link samples with a scientist's sample request.   |
|                            | s_c_sampling_code      | Code used to identify samples taken for a sample request. Used with s_c_leg.  |
|                            | sam_archive_working    | Part of section where sample was taken. Valid values: WR – whole round, A – archive half, W – working half.   |
|                            | top_interval           | Distance in meters from the top of the section to the top of the sample.  |
|                            | bottom_interval        | Distance in meters from the top of the section to the bottom of the sample.   |

## Gas Chromatography

| Table Name | Column Name         | Column Comment  |
|------------|---------------------|---|
|            | piece               | Additional identifier for hard rock samples. Each individual piece of rock within a section is numbered consecutively starting at the top of the section.   |
|            | sub_piece           | Additional identifier for hard rock samples. When a piece is broken, the individual fragments are given consecutive letter designations. Note that subpiece assignments must be made in conjunction with piece numbers. |
|            | beaker_id           | The number on the moisture density beaker. Used for samples analyzed for moisture and density.  |
|            | volume              | Volume of sample.   |
|            | entered_by          | Indicates who entered the sample into the database.   |
|            | sample_depth        | Depth of the sample.  |
|            | sample_comment      | Comment about the sample.   |
|            | sam_repository      | Repository where sample was taken. Valid values SHIP (ship), GCR (Gulf Coast Repository), ECR (East Coast Repository), WCR (West Coast Repository) and BCR (Bremen Core Repository).                                    |
|            | sam_sample_code_lab | Code to indicate the shipboard lab that will perform the initial analysis.  |
|            | sam_section_id      | Unique Oracle-generated sequence number to identify each section. This is a foreign key that links a sample to leg, site, hole, core, and section.  |
|            | timestamp           | Date and time when sample was entered into database. Samples taken before November 25, 1998 and migrated samples have the timestamp 11/25/1998 12:26PM.   |

## Appendix II. Description of items from Gas Elements query

| <b>Item Name</b>                   | <b>Column Description and Calculations</b>   | <b>Format</b>       |
|------------------------------------|--|---------------------|
| Leg                                | Number identifying the cruise. The ODP started numbering the scientific cruises of the <i>JR</i> at Leg 101. A leg was nominally two months duration. During the 18+ years of the ODP, there were 110 cruises on the <i>JR</i> .   | Integer 3           |
| Site                               | Number identifying the site. A site is the location where one or more holes were drilled while the ship was positioned over a single acoustic beacon. The <i>JR</i> visited 656 unique sites during the course of the ODP. Some sites were visited multiple times, including some sites originally visited during the Deep Sea Drilling Program for a total of 673 site visits.  | Integer 4           |
| Hole                               | Letter identifying the hole. Multiple holes could be drilled at a single site by pulling the drill pipe above the seafloor, moving the ship some distance away and drilling another hole. The first hole was designated 'A' and additional holes proceeded alphabetically at a given site. Location information for the cruise was determined by hole latitude and longitude. During ODP, there were 1818 holes drilled or deepened. | Text 1              |
| Core                               | Cores are numbered serially from the top of the hole downward. Cored intervals are up to 9.7 m long, the maximum length of the core barrel. Recovered material was placed at the top of the cored interval, even when recovery was less than 100%. More than 220 km of core were recovered by the ODP.   | Integer 3           |
| Type                               | All cores are tagged by a letter code that identifies the coring method used.  | Text 1              |
| Section                            | Cores are cut into 1.5 m sections in order to make them easier to handle. Sections are numbered serially, with Section 1 at the top of the core. Gas analyses were made on samples taken from the sections. Core Catcher sections identified as "CC."  | Integer 2 or Text 2 |
| Top (cm)                           | The top interval of a measurement in centimeters measured from the top of a section.   | Decimal F4.1        |
| Bottom (cm)                        | The location of the bottom of a sample in centimeters measured from the top of a section.  | Decimal F4.1        |
| Depth (mbsf)                       | Distance in meters from the seafloor to the sample location.   | Decimal F7.3        |
| Methane/Ethane (C1/C2 ratio)       | Methane to Ethane ratio – C1 / C2  | Decimal F15.5       |
| Methane (C1) [ppm]                 | Methane results in parts per million.  | Decimal F15.5       |
| Ethane (C2) [ppm]                  | Ethane results in parts per million.   | Decimal F15.5       |
| Ethylene (C2=) [ppm]               | Ethylene results in parts per million.   | Decimal F15.5       |
| Ethane + Ethylene (C2+C2=) [ppm]   | Sum of Ethane and Ethylene in parts per million.   | Decimal F15.5       |
| Propane (C3) [ppm]                 | Propane results in parts per million.  | Decimal F15.5       |
| Propane + Propylene (C3+C3=) [ppm] | Sum of Propane and Propylene in parts per million.   | Decimal F15.5       |
| Propylene (C3=) [ppm]              | Propylene results in parts per million.  | Decimal F15.5       |
| i-Butane (I-C4) [ppm]              | i-Butane results in parts per million.   | Decimal F15.5       |
| n-Butane (N-C4) [ppm]              | n-Butane results in parts per million.   | Decimal F15.5       |
| n-Pentane (N-C5) [ppm]             | n-Pentane results in parts per million.  | Decimal F15.5       |

| <b>Item Name</b>             | <b>Column Description and Calculations</b>  | <b>Format</b> |
|------------------------------|---|---------------|
| i-Pentane (I-C5) [ppm]       | i-Pentane results in parts per million.   | Decimal F15.5 |
| n-Hexane (N-C6) [ppm]        | n-Hexane results in parts per million.  | Decimal F15.5 |
| i-Hexane (I-C6) [ppm]        | i-Hexane results in parts per million.  | Decimal F15.5 |
| n-Heptane (N-C7) [ppm]       | n-Heptane results in parts per million.   | Decimal F15.5 |
| i-Heptane (I-C7) [ppm]       | i-Heptane results in parts per million.   | Decimal F15.5 |
| Nitrogen (N2) [ppm]          | Nitrogen results in parts per million.  | Decimal F15.5 |
| Oxygen (O2) [ppm]            | Oxygen results in parts per million.  | Decimal F15.5 |
| Hydrogen Sulfide (H2S) [ppm] | Hydrogen Sulfide results in parts per million.  | Decimal F15.5 |
| Carbon Dioxide (CO2) [ppm]   | Carbon Dioxide results in parts per million.  | Decimal F15.5 |
| Run                          | Oracle-generated run ID   | Integer 9     |
| Instrument                   | Instrument that analysis was done on. Valid values:<br>CAR – Carle Gas Chromatograph<br>GC1 – HP Gas Chromatograph 5890A<br>GC2 – HP Gas Chromatograph 5890A<br>GC3 – HP Gas Chromatograph 5890 Series II<br>NGA – Natural Gas Analyzer | Text 10       |
| Method                       | Sampling method. HS – headspace, VAC - vacutainer   | Text 3        |
| Detector                     | Type of detector used for the analysis: Valid values:<br>FID – Flame Ionization Detector<br>TCD – Thermal Conductivity Detector   | Text 3        |